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Vibrational spectra, thermodynamic functions and barrier to internal rotation of 2-chloro-5-nitropyridine

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Abstract : The infrared spectrum of 2-chloro-5-nitropyridine in the range 4000–50 cm^{-1} in the polycrystalline state and the polarized laser Raman spectrum of the melt of the substance have been measured. A complete vibrational assignment of the observed frequencies is presented. The torsional frequency of the NO_2 group has been identified at 67 cm^{-1} corresponding to a potential barrier of 4.99 K cal mol^{-1} hindering the free rotation of the NO_2 group. Ideal gas state thermodynamic functions of the molecule are determined in the temperature range 273.1–1500 K.

Keywords : Infrared spectrum, Raman spectrum, thermodynamic functions.

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As an extension of the earlier studies of the vibrational spectra of a few substituted pyridines [1-4] the infrared and Raman spectra of 2-chloro-5-nitropyridine have been investigated in this work. It appears that there is no earlier report on the vibrational spectrum of this molecule. The present paper deals with a detailed study of the infrared and polarized Raman spectra of 2-chloro-5-nitropyridine. A complete vibrational assignment of the observed frequencies based on the state of polarization of the Raman lines and comparison with the assignments proposed for related molecules is presented. The ideal gas state thermodynamic functions of the molecule are also computed in the temperature range 273.1–1500 K by utilising the observed fundamental frequencies assuming a rigid-rotor and harmonic-oscillator approximation. The relevancy of this study is seen from the fact that the heterocyclic compounds are finding increasing applications in a diverse variety of fields. So the physical properties of these compounds must be thoroughly studied. In view of this, a knowledge of

the thermodynamic quantities seemed desirable. The state of polarization of the Raman line was studied by the same method described elsewhere [5].

The observed infrared and Raman frequencies of 2-chloro-5-nitropyridine together with their relative intensity, depolarization ratio of the Raman lines and probable assignments

Table 1. Observed infrared and Raman frequencies and assignments for 2-chloro-5-nitropyridine.

Infrared (cm^{-1}) Pellet	Raman (cm^{-1}) Melt	ρ^*	Assignment
3150 (w)	3140 (w)	0.02	$\nu_4 + \nu_5 (A')$
3127 (w)			$2 \times \nu_5 (A')$
3094 (mw)	3100 (sh)	*p*	$\nu_1 (a')$, 20*b*
	3076 (ms)	0.27	$\nu_2 (a')$, 2
3050 (ms)			$\nu_3 (a')$, 20*a*
1592 (vs)	1594 (sh)	*p*	$\nu_4 (a')$, 8*a*
1563 (s)	1566 (vs)	0.24	$\nu_5 (a')$, 8*b*
1514 (s)	1526 (mw)	*p*	$\nu_6 (a')$, $-NO_2$ asymmetric stretch
1443 (s)	1463 (mw)	0.48	$\nu_7 (a')$, 19*a*
1420 (mw)	1420 (mw)	0.29	$\nu_8 (a')$, 19*b*
1380 (ms)	1384 (w)	0.26	$\nu_{21} + \nu_{23} (A')$
1352 (vs)	1350 (vs)	0.02	$\nu_9 (a')$, $-NO_2$ symmetric stretch
1273 (ms)	1276 (mw)	0.15	$\nu_{10} (a')$, 14
1254 (ms)	1252 (mw)	0.03	$\nu_{11} (a')$, 3
1228 (mw)			$\nu_{21} + \nu_{27} (A')$
1136 (ms)	1143 (mw)	0.2	$\nu_{12} (a')$, 15
1115 (s)	1108 (s)	0.12	$\nu_{13} (a')$, 13
1061 (w)	1060 (w)	0.03	$\nu_{14} (a')$, 18*a*
1014 (ms)	1015 (w)		$\nu_{15} (a')$, 1
995 (mw)			$\nu_{16} (a')$, 17a
946 (ms)	937 (w)		$\nu_{17} (a')$, 5
860 (s)	859 (s)	0.09	$\nu_{18} (a')$, $-NO_2$ symmetric deformation
820 (sh)			$\nu_{19} (a'')$, 12
792 (vw)			$\nu_{20} (a'')$, 10*b*
751 (s)	750 (mw)	0.37	$\nu_{21} (a')$, 7*b*
710 (mw)	715 (w)		$\nu_{22} (a'')$, 4
629 (ms)	624 (mw)	0.67	$\nu_{23} (a')$, 6*b*
611 (w)			$\nu_{24} (a')$, 6*a*
531 (s)	528 (w)		$\nu_{25} (a'')$, $-NO_2$ out-of-plane wag
473 (ms)			$\nu_{26} (a'')$, 11
			$\nu_{27} (a')$, $-NO_2$ in-plane rocking

Table 1. (*Cont'd.*)

Infrared (cm^{-1}) Pellet	Raman (cm^{-1}) Melt	ρ^*	Assignment
411 (ms)	412 (w)		ν_{28} (a''), 16*a*
343 (mw)	342 (w)	*p* ?	ν_{29} (a'), 9*a*
321 (mw)	318 (mw)	0.1	ν_{30} (a'), 18*b*
274 (ms)	272 (mw)	0.6	ν_{31} (a''), 10*a*
196 (ms)	198 (w)	*dp*	ν_{32} (a''), 16*b*
104 (ms)			Lattice mode
67 (ms)			ν_{33} (a''), $-NO_2$ torsion

ρ^* = Depolarization ratio.

Frequencies observed in the region 3000–1600. cm^{-1} in solid thin film :

2968 (w) :	$\nu_6 + \nu_7$ (A');	2934 (mw) :	$\nu_6 + \nu_8$ (A');	2863 (mw) :	$\nu_6 + \nu_9$ (A');
2714 (w) :	$\nu_7 + \nu_{10}$ (A');	2630 (w) :	$\nu_6 + \nu_{13}$ (A');	2588 (vw) :	$\nu_7 + \nu_{12}$ (A');
2512 (w) :	$\nu_7 + \nu_{14}$ (A');	2291 (w) :	$\nu_8 + \nu_{18}$ (A');	2269 (w) :	$\nu_{11} + \nu_{15}$ (A')
2130 (w) :	$\nu_{10} + \nu_{18}$ (A');	2103 (w) :	$\nu_9 + \nu_{21}$ (A');	1988 (mw) :	$2\nu_{16}$ (A'), $\nu_6 + \nu_{27}$ (A');
1885 (mw) :	$2\nu_{17}$ (A');	1860 (w) :	$\nu_{13} + \nu_{21}$ (A');	1709 (mw) :	$\nu_{16} + \nu_{22}$ (A')
1657 (mw) :	$\nu_{17} + \nu_{22}$ (A').				

Table 2. Thermodynamic functions of 2-chloro-5-nitropyridine*.

Temperature K	C_p^0 cal K^{-1} mol^{-1}	$\left(H^0 - E_0^0\right)/T$ cal K^{-1} mol^{-1}	S^0 cal K^{-1} mol^{-1}	$-\left(F^0 - E_0^0\right)/T$ cal K^{-1} mol^{-1}
273.1	28.01	16.46	84.58	68.13
298.1	30.18	17.52	87.13	69.61
300	30.34	17.60	87.32	69.72
400	38.20	21.80	97.15	75.36
500	44.53	25.73	106.40	80.65
600	49.47	29.30	115.00	85.67
700	53.31	32.46	122.90	90.43
800	56.34	35.27	130.20	94.95
900	58.77	37.75	137.00	99.25
1000	60.74	39.95	143.30	103.30
1100	62.36	41.92	149.20	107.20
1200	63.70	43.68	154.60	111.00
1300	64.84	45.26	159.80	114.50
1400	65.79	46.70	164.60	117.90
1500	66.61	48.00	169.20	121.20

* Ideal gas state at standard pressure of 1 atom.

are given in Table 1. In Table 2 are listed the calculated values of the thermodynamic functions. The polarized Raman spectrum is reproduced in Figure 1.

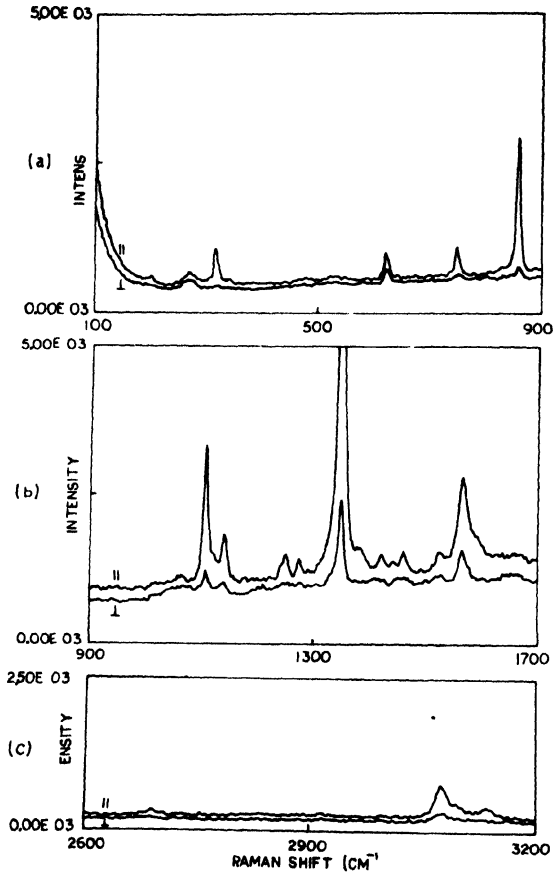

Figure 1 (a), (b) and (c). Polarized laser Raman spectrum of 2-chloro-5-nitropyridine in the liquid state just above the melting point.

Assuming that the NO_2 group is in the plane of the ring, the molecular symmetry of 2-chloro-5-nitropyridine is taken to be C_s and the thirty-three normal modes divide according to $\Gamma = 23\,a' + 10\,a''$. The Raman line falling into a' species should be polarized while that belonging to a'' species depolarized.

Species a':

The three C–H stretching frequencies are identified with the observed infrared bands at 3094 and 3050 cm^{-1} and the polarized Raman line at 3076 cm^{-1}. The polarized Raman shifts at 1594, 1566,1463, 1420 and 1276 cm^{-1} are assigned as the a' fundamentals arising essentially from the ring carbon stretching modes. Strong infrared absorption bands are observed at 1115 and 751 cm^{-1}, their Raman counterparts at 1108 and 750 cm^{-1} respectively being highly

polarized. These are assigned to the substituent-sensitive a' modes involving essentially the stretching of the C–N and C–Cl bonds respectively in agreement with the previous assignments [3,6-8]. The two components of the planar ring bending mode are identified with the polarized Raman line at 624 cm^{-1} ($\rho = 0.67$) and the infrared absorption observed at 611 cm^{-1}. The remaining a' fundamentals that may be derived from pyridine are assigned to the polarized Raman lines at 1252, 1143, 1060, 342 and 318 cm^{-1} and the infrared bands of medium strength at 1014 and 820 cm^{-1}.

Species a":

The two substituent-sensitive modes belonging to the a'' species are identified with the depolarized Raman line at 198 cm^{-1} and the nearly depolarized Raman line observed at 272 cm^{-1}. The moderately intense infrared bands are observed at 710 and 473 cm^{-1}, the corresponding Raman line is weak or absent. They are assigned as a'' fundamentals arising principally from the out-of-plane deformation of the ring carbon atoms and the hydrogen atoms respectively. Other a'' modes may be identified with the infrared bands at 995, 946, 792 and 411 cm^{-1}. These assignments are in agreement with those proposed for the related molecules [1,3,9-12].

The internal vibrations of the NO_2 group:

The symmetric and asymmetric stretching and symmetric deformation frequencies of the NO_2 group are unambiguously assigned [13,14]. The infrared bands observed at 531 and 473 cm^{-1} may arise from the NO_2 out-of-plane wagging and in-plane rocking modes respectively. These assignments are in agreement with those proposed for nitropyridines [12] and nitrobenzene [8,15,16]. A medium strong infrared band is observed at 67 cm^{-1} in the polycrystalline state. A similar band was observed at 73.3 cm^{-1} in the case of liquid 2-fluro-5-nitropyridine (unpublished work) which was assigned to the torsional frequency of the NO_2 group. Moreover, the NO_2 torsional frequency in nitrobenzene has been suggested at 70 cm^{-1} [17,18]. On this basis, the band at 67 cm^{-1} in the present case is tentatively assigned to the NO_2 torsional mode which gives a potential barrier of 4.99 K cal/mole. Of course, the confirmation of the assignment would come from the measurement of the infrared band in the liquid state of solution phase in the present case.

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